

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
26 April 2001 (26.04.2001)

PCT

(10) International Publication Number  
**WO 01/28972 A1**

- (51) International Patent Classification<sup>7</sup>: C07C 67/38, 69/54, 69/618, 69/533
- (21) International Application Number: PCT/EP00/10427
- (22) International Filing Date: 20 October 2000 (20.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
99308353.4 22 October 1999 (22.10.1999) EP
- (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): DRENT, Eit [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). PRINGLE, Paul, Gerard [GB/GB]; Cantocks Close, Bristol, Avon BS8 1TS (GB). PUGH, Robert, Ian [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).
- (74) Agent: ZEESTRATEN, Albertus, Wilhelmus, Joannes; Shell International B.V., Intellectual Property Services, P.O. Box 384, NL-2501 CJ The Hague (NL).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE CARBONYLATION OF AN ACETYLENICALLY UNSATURATED COMPOUND

(57) Abstract: Process for the carbonylation of an acetylenically unsaturated compound by reaction with carbon monoxide and a co-reactant in the presence of a catalyst system based on (a) a source of platinum; (b) a source of anions and (c) a diphosphine of the following formula (1)  $R^1 > P-R^2-PR^3R^4$  wherein  $R^2$  represents a covalent bridging group,  $R^1$  represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group), and wherein  $R^3$  and  $R^4$  independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms.

WO 01/28972 A1

PROCESS FOR THE CARBONYLATION OF AN ACETYLENICALLY  
UNSATURATED COMPOUND

The invention is related to a process for the carbonylation of an acetylenically unsaturated compound by reaction with carbon monoxide and a co-reactant in the presence of a catalyst system based on (a) a source of platinum; (b) a source of anions and (c) a diphosphine. The invention is especially directed to a process in which linear carbonylation products are selectively prepared.

In view of the fact that for a number of outlets the availability of linear, rather than branched carbonylated products would be desirable, e.g. in the preparation of components of detergent compositions, efforts have been made to increase the selectivity with respect to linear carbonylation products. WO-A-9421585 describes a process, wherein use is made of a catalyst system based on platinum, a bisphosphine ligand and a source of anions, typically a strong acid. A disadvantage of this process is that the activity of this catalyst system is somewhat low, being in the order of 20 to 200 mole product per mole Pt per hour for acetylene as reactant.

A process having a higher catalyst activity is known from WO-A-9720803. A carbonylation of ethylene with carbon monoxide and t-butyl alcohol is described using a catalyst system consisting of 1,2-P,P'-bis(9-phosphabicyclononyl)ethane as the ligand, platinum(II)(acetylacetonate)<sub>2</sub> as the platinum source, methane sulphonic acid as the anion source, SnCl<sub>2</sub> and 2,5,8-tri-oxanonane.

A disadvantage of this process is that SnCl<sub>2</sub> has to be present in order to achieve an acceptable activity and selectivity. The use of SnCl<sub>2</sub> is not preferred because

when performing this process in a continuous manner  $\text{SnCl}_2$  will be lost due to alcoholysis. This is not desirable because new  $\text{SnCl}_2$  has to be added and the tin alkoxide formed will have to be discharged resulting in obvious environmental problems. Furthermore when tin alkoxide is removed from the process by means of a purge additional catalyst will be lost. It is therefore highly desirable to perform such a carbonylation process in the absence of tin chloride compounds like  $\text{SnCl}_2$ .

US-A-5719313 describes the carbonylation of propyne with CO and methanol using a catalyst system consisting of palladium (II) acetate, bisphenyl(2-pyridyl)phosphine and methanesulfonic acid. A disadvantage of this process is that the mono phosphine ligand is consumed in the process by 'quarternization' of the ligand with the acrylate product. A further disadvantage of this process is that mostly branched products are formed.

WO-A-9842717 describes the carbonylation of ethene with carbon monoxide and methanol in the presence of a catalyst system consisting of platinum (II) (acetyl-acetate)<sub>2</sub>, 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl]propane and methanesulphonic acid. The publication does not disclose that acetylenically unsaturated compounds can be carbonylated using such a catalyst system.

The object of the present invention is a process for the carbonylation of acetylene to linear products, which process can be performed in the absence of  $\text{SnCl}_2$ . Such a process is described below. Process for the carbonylation of an acetylenically unsaturated compound by reaction with carbon monoxide and a co-reactant in the presence of a catalyst system based on (a) a source of platinum; (b) a source of anions and (c) a diphosphine of the following formula



wherein  $R^2$  represents a covalent bridging group,  $R^1$  represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group), and wherein  $R^3$  and  $R^4$  independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms.

With the above process the carbonylation can be performed with a good turn over rate, a high selectivity to the desired carbonylation products and in the absence of  $SnCl_2$ . It has furthermore been found that the ligand is stable over a prolonged period of time making it very suitable for use in a continuously operated commercial application.

Tricyclo[3.3.1.1{3,7}]decane is the systematic name for a compound more generally known as adamantane. Therefore, the optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group will be referred to as "2-PA" group (as in 2-phosphadamantyl group) throughout the specification.

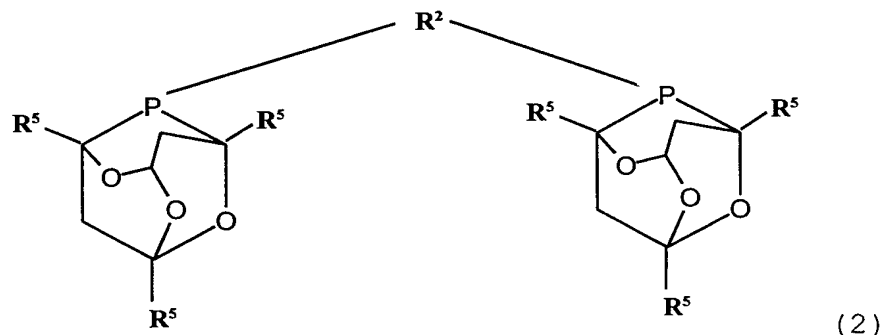
The 2-PA group has preferably additional heteroatoms other than the 2-phosphorus atom in its skeleton. Suitable heteroatoms are oxygen and sulphur atoms. Suitably, these heteroatoms are found in the 6, 9 and 10 positions. The most preferred bivalent radical is the 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group. Preferably, the 2-PA group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical  $R^5$  of up to 20 atoms. Typical examples of  $R^5$  include methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl. More preferably, the 2-PA group is

substituted on each of the 1, 3, 5 and 7 positions,  
suitably with identical radicals  $R^5$ .

Each of the monovalent radicals  $R^3$  and  $R^4$  may inde-  
pendently be selected from (substituted) hydrocarbyl  
groups such as, for instance, methyl, phenyl, pyridyl, or  
o,o-di(t-butoxy)phenyl, and (substituted) heterohydro-  
carbyl groups such as, for instance, trimethylsilyl or  
alkoxy groups. Alternatively,  $R^3$  and  $R^4$  may together form  
a bivalent radical, such as 1,6-hexylene, 1,3 or  
1,4-cyclooctylene. Preferably,  $R^3$  and  $R^4$  together with  
the phosphorus atom form a 2-PA group. Most preferably  $R^2$   
connects two identical 2-PA groups.

The bridging group  $R^2$  can be an organic bivalent  
group having up to 20 atoms. Examples of such bridging  
groups are ferrocenyl and nickelocenyle. Preferably  $R^2$   
has 2 to 4 atoms in the shortest chain of atoms directly  
connecting the two phosphorus atoms. Most preferably the  
number of atoms in the shortest chain of atoms directly  
connecting the two phosphorus atoms is 3. Preferably the  
atoms in the chain are carbon atoms. Examples of  
preferred bridging groups are ortho xylyl, ethylene and  
tri-methylene groups.

A suitable example of such a ligand is one according  
to the following general formula:



in which  $R^5$  and  $R^2$  can be as describes above.

Examples of ligands which may be used in the process  
according to the invention are exemplified in the above

cited WO-A-9842717. Most preferably 1,2-P,P'-di(2-phos-  
pha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-  
[3.3.1.1{3.7}decyl)ethane (DPA2) and 1,3-P,P'-  
5 di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatri-  
cyclo[3.3.1.1{3.7}decyl)propane (DPA3) are used.

For the preparation of the catalyst system to be used  
in the process of the invention, the amount of bidentate  
ligand is suitably applied in some excess of the amount  
of platinum, expressed as moles of bidentate ligand per  
10 mole atom of platinum. The active species, however, is  
believed to be based on an equimolar amount of bidentate  
ligand per mole platinum. Thus, the molar amount of  
bidentate ligand per mole of platinum is suitably in the  
range of 1 to 3, preferably in the range of 1 to 2.

15 As regards the source of platinum, i.e.,  
component (a) of the catalyst system, any platinum  
compound allowing complexing between the metal and the  
bidentate ligand may be used. Suitable compounds are for  
instance, metallic platinum, zerovalent platinum  
20 complexes, such as tetrakis(triphenylphosphine)platinum;  
and tetra- or divalent platinum salts. In particular  
platinum(II) salts are suitable, such as dipotassium  
tetracyanoplatinate, disodium tetracyanoplatinate,  
dipotassium tetrachloroplatinate, potassium trichloro  
25 (ethylene) platinate, sodium trichloro (ethylene)  
platinate, platinum-bis(cyanobenzene) disulphate and  
platinum-bis(triphenylphosphine) disulphate. Salts of  
platinum with carboxylic acids, in particular with  
carboxylic acids having from 2 to 12 carbon atoms, are  
30 also suitable, for example platinum diacetate, platinum  
dipropionate and platinum dihexanoate. Organic  
platinum(II) complexes are preferably applied as source  
of platinum, platinum(II) acetylacetonate being  
particularly suitable.

The molar amount of anion per mole of platinum is conveniently selected in the range of 1 to 12. Preferably the anion is applied in a molar amount per mole of platinum in the range of 1 to 8.

5       The process of the invention is carried out with catalytic amounts of the catalyst system, i.e. per mole of acetylenically unsaturated compound,  $10^{-8}$  to  $10^{-1}$  mole of platinum is present, preferably from  $10^{-7}$  to  $10^{-2}$ , on the same basis.

10       The catalyst systems used in the process of the invention comprises further a source of anions as component (b). It is believed that the size of the anion and the distribution of electric charge in the anion significantly contribute to the stability of the catalyst  
15       system. Preferably, anions are used that are the conjugated base of acids having a pKa (measured at 18 °C in water) of less than 4. Suitable anions include anions derived from Bronsted acids, in particular from  
20       carboxylic acids, such as 2,6-dichlorobenzoic acid, and 2,6-bis(trifluoromethyl)benzoic acid or trifluoroacetic acid; and from sulphonic acids, such as methanesulphonic acid, and trifluoromethanesulphonic acid.

25       The acetylenically unsaturated compounds which may suitably be employed as starting material in the process of the invention, include compounds containing from 2 to 20 carbon atoms, optionally containing one or more inert substituents, such as halogen atoms or hydroxygroups. Preferably, the acetylenically unsaturated compounds has from 2 to 8 carbon atoms per molecule. The acetylenically  
30       unsaturated bond is usually the only carbon-carbon unsaturation in the molecule. In view of the envisaged preparation of mainly linear carbonylated products, it is preferably located at a terminal position. Examples of suitable acetylenically unsaturated compounds are  
35       acetylene(= ethyne), methylacetylene (= propyne),

1-butynes, 1-pentyne, 1-hexyne, 1-octyne, phenylacetylene and 3-hydroxybutyne. Acetylene is most preferred.

Suitable co-reactants in the process of the invention are hydrogen-containing compounds whereby a carbon monoxide molecule and at least one acetylenically unsaturated compound can be inserted into the bond between the hydrogen atom and the molecule of the co-reactant. Examples thereof include nucleophilic compounds containing at least one mobile hydrogen atom.

Preferred nucleophilic compounds include: water and alcohols, e.g., monohydric alcohols, such as methanol, ethanol, isopropanol and 1-butanol, and polyhydric alcohols, such as ethyleneglycol, 1,4-butanediol and glycerol; thiols; primary or secondary amines or amides; phenols and carboxylic acids, for example acetic acid, pivalic acid and propionic acid. Monohydric alcohols having from 1 to 6 carbon atoms are preferred, in particular methanol and butanol.

Another category of suitable co-reactants comprises hydride sources such as molecular hydrogen and compounds capable of generating molecular hydrogen. In particular for embodiments of the process whereby an acetylenically unsaturated compound is hydroformylated, molecular hydrogen is a preferred co-reactant.

Finally, also a combination of a nucleophilic compound and a hydride source as defined above may be used, to prepare a carbonylation-hydroformylation product.

The carbonylation process of the invention is generally carried out at a reaction temperature in the range of 40 to 200 °C, more suitably at a temperature in the range of 50 to 160 °C.

The total reaction pressure is usually in the range of 5 to 150 bar absolute (bara). Pressures between 10 and 80 bara and in particular between 30 and 60 bara are



preferred. In carbonylation reactions of the hydro-  
formylation type, the total pressure is usually the sum  
of the partial pressures of carbon monoxide and hydrogen.  
The molar ratio between these gases may vary, but is  
5 conveniently maintained in the range of 1:2 to 2:1.  
Preferably, substantially equimolar amounts of carbon  
monoxide and hydrogen are used. In other carbonylation  
reactions, involving no hydrogen, or only insignificant  
amounts thereof, the total pressure is roughly the same  
10 as the carbon monoxide pressure.

The process of the invention may be carried out in  
the absence of a separate diluent or solvent, if so  
desired. However, it is often convenient to have a liquid  
diluent or solvent present at the beginning of the  
15 reaction, e.g. if a volatile acetylenic starting material  
is used, or if the reaction requires a relatively long  
induction period and continued thorough mixing of the  
reactants is desirable. Suitable solvents are, in  
particular, aprotic compounds such as ethers or ketones,  
20 for example 2,5,8-trioxanonane, diethylether, acetone,  
diglyme and methyl ethylketone.

The invention is further illustrated by the following  
non-limiting examples.

#### Example 1

25 (a) A 250 ml "Hastelloy C" (trademark) magnetically  
stirred autoclave was charged with acetylene (1.4 bara),  
30 ml of 1-propanol, 0.1 mmol of Pt(acac)<sub>2</sub>, 0.12 mmol of  
DPA-3 ligand (see above), 0.25 mmol of methyl sulfonic-  
acid and 30 ml diglyme as solvent.

30 The autoclave was pressurised with 40 bara carbon  
monoxide and then sealed. The temperature of the mixture  
was raised to 115 °C. Complete conversion of acetylene  
was reached in shorter than 30 minutes at 115 °C and  
Glc analysis after cooling and depressurizing, showed a  
35 selectivity of 90 mol% to propyl acrylate. A propyl

acrylate formation rate of about 2000 t.o./hr/  
mol Pt was calculated. Some byproducts are succinate and  
malonate diesters; these are due to consecutive  
carbonylation of acrylate at complete acetylene  
conversion. In a commercial operation the selectivity  
will be higher by keeping the acetylene conversion per  
pass below the 100%.

#### Example 2

Example 1 was repeated except that the co-reactant  
was 30 ml methanol and that as acetylenically unsaturated  
compound 10 ml phenyl acetylene was used. The reaction  
time was 1 hour. A phenyl acrylate formation rate of  
1000 turnovers per hour per mol Pt was calculated. The  
products consisted of 52% of linear 3-phenyl acrylate and  
48% of 2-phenyl acrylate.

#### Example 3

Example 2 was repeated except that as acetylenically  
unsaturated compound 10 ml 1-pentyne was used. The  
reaction time was 1 hour. A pentyne consumption rate of  
300 turnovers per hour per mol Pt was calculated. The  
products consisted of 65% of linear methyl 2-hexenoate  
and 35% of 2-methyloxy carbonyl 1-pentene.

Example 1 was repeated except that the co-reactant  
was 30 ml methanol and that as acetylenically unsaturated  
compound 10 ml phenyl acetylene was used. The reaction  
time was 1 hour. A phenyl acrylate formation rate of  
1000 turnovers per hour per mol Pt was calculated. The  
products consisted of 52% of linear 3-phenyl acrylate and  
48% of 2-phenyl acrylate.

#### Example 4

Example 1 was repeated except that as ligand DPA-2  
(see above) was used and as co-reactant 30 ml methanol. A  
methyl acrylate formation rate of about 290 t.o./hr/(mol  
Pt) was calculated. The reaction time was one hour and  
the selectivity towards methyl acrylate was 76 wt%.

C L A I M S

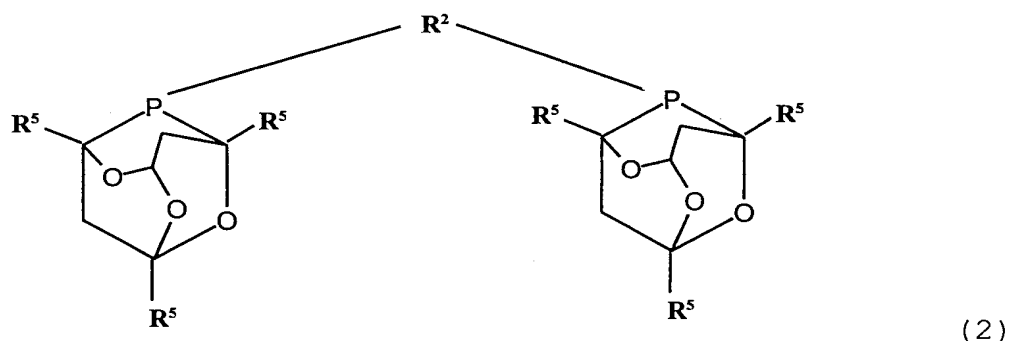
1. Process for the carbonylation of an acetylenically unsaturated compound by reaction with carbon monoxide and a co-reactant in the presence of a catalyst system based on (a) a source of platinum; (b) a source of anions and  
5 (c) a diphosphine of the following formula



wherein  $R^2$  represents a covalent bridging group,  $R^1$  represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally  
10 substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group), and wherein  $R^3$  and  $R^4$  independently represent univalent radicals of up to 20 atoms or jointly form a bivalent  
15 radical of up to 20 atoms.

2. Process according to claim 1, wherein  $R^3$  and  $R^4$  together with the phosphorus atom to which it is attached form a 2-PA group identical to the group formed by  $R^1$  together with the phosphorus atom to which it is  
20 attached.

3. Process according to claim 2, wherein the 2-PA group is a 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group according to the following general formula:



in which  $R^5$  is monovalent radical of up to 20 atoms.

4. Process according to claim 3, wherein  $R^5$  is a radical selected from methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl.

5. Process according to any one of claims 1-4, wherein  $R^2$  has 2 to 4 atoms in the shortest chain of atoms directly connecting the two phosphorus atoms.

6. Process according to any one of claims 1-5, wherein the acetylenically compound has from 2 to 8 carbon atoms.

7. Process according to claim 6, wherein the acetylenically compound is acetylene.

8. Process according to any one of claims 1-7, wherein the co-reactant is a monohydric alcohols having from 1 to 6 carbon atoms.

9. Process according to any one of claims 1-8, wherein the source of anions is the conjugated base of acids having a  $pK_a$ , as measured at 18 °C in water, of less than 4.

10. Process according to claim 9, wherein the acid is methanesulfonic acid.

# INTERNATIONAL SEARCH REPORT

Inter. ☐ National Application No

PCT/EP 00/10427

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C67/38 C07C69/54 C07C69/618 C07C69/533

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 42717 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 1 October 1998 (1998-10-01) cited in the application page 1, line 22 -page 2, line 31 page 3, line 8 - line 21 page 13 -page 15; claims -----	1
A	WO 94 21585 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 29 September 1994 (1994-09-29) cited in the application page 2, line 19 -page 3, line 2 page 11 -page 13; claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

16 January 2001

Date of mailing of the international search report

26/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Kinzinger, J

# INTERNATIONAL SEARCH REPORT

...information on patent family members

International Application No

PCT/EP 00/10427

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9842717 A	01-10-1998	AU 7428498 A EP 0971940 A US 6156934 A ZA 9802476 A	20-10-1998 19-01-2000 05-12-2000 23-03-1998
WO 9421585 A	29-09-1994	CN 1119433 A,B DE 69408571 D DE 69408571 T EP 0689529 A ES 2112533 T JP 8507778 T SG 47664 A US 5414109 A	27-03-1996 26-03-1998 04-06-1998 03-01-1996 01-04-1998 20-08-1996 17-04-1998 09-05-1995